ABSTRACT

This report contains the studies done to investigate the natural sequestration of carbon dioxide gas in seawater and the temperature effects towards the formation of calcium carbonate in forms of calcite and aragonite. Early studies done reveals that it is believed that carbon dioxide gas released in the atmosphere actually is one of the causes of the global warming phenomenon. Apart from that, the study uses literature reviews as well as relevant theories from previously done experiment, providing a great guidelines and reference for the study. The experiments were constructed from information gained from well-established theories from the literatures and then executed with objectives of verifying the existing, as well as investigating the relationship of temperature variation towards the formation of calcium carbonate from the actual seawater whether or not aragonite and calcite were present and in what manner it did. The experiment was actually divided into two main sections; one using the artificial seawater as the main reagent and the other one is using actual seawater as the main reagent. The experiments actually yield positive results in which aragonite and calcite were formed, and later confirmed with the Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) analysis done as the characterization procedure. From the results, detailed analysis were done to study the pattern of formation of calcium carbonate at different temperature, where the formation of calcite is favored at lower temperature (30°C) and aragonite and higher temperature (70°C). At temperature of 50°C and 70°C, presence of both aragonite and calcite were detected. In addition, during the analysis, the presence of calcium carbonate in forms of vaterite was detected. Conclusively, the experiments successfully proved that carbon dioxide can actually sequestrate naturally in seawater and temperature is one of the manipulating variables than influences it in a manner that calcite and aragonite forms at each different temperature level.

ACKNOWLEDGEMENT

First and foremost, thank God, that with His will and guidance, I can finish my thesis successfully despite all the difficulties encountered. I would like to thank my supervisor Associate Professor Dr. Mohamed Ibrahim Abdul Mutalib at the Universiti Teknologi PETRONAS from the Chemical Department for his excellent guiding, help and supports in my work with this thesis. I would also like to thank Prof. Dr. Bernard J. Pierson for giving me great support and interest that later leads towards the completion of the study. My thanks also go to my colleague Mohd. Akram Said for valuable discussions while working with this thesis. Finally, I would like to thank all fellow lab technicians from the Chemical Engineering Department and Mechanical Engineering Department, for their knowledge and skills. Without all of the mentioned technical expertise and assistance, this would not be a great and impactful thesis. The knowledge gained from the study is hoped to greatly benefits mankind in the future.

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CHAPTER 1

INTRODUCTION

1.1 Background Studies

In 2008, there was an interesting finding by researcher Barbara Lidz and Helen Gibbons regarding the formation of calcium carbonate, $CaCO_3$ in the Persian Gulf [1]. Some portions of $CaCO_3$ formed were being washed away towards the shallower part of the ocean by the waves. The white precipitates formed were identified as $CaCO_3$ in forms of aragonite. With regards to the phenomenon, it is believed that the local climate is the main factor that induces the formation process. High temperature might be the cause of the formation of $CaCO_3$ precipitate from the seawater. Figure 1.1 shows the evidence of the formation of $CaCO_3$ in the Persian Gulf, where the faded area in the sea as shown in the figure was further identified as aragonite.

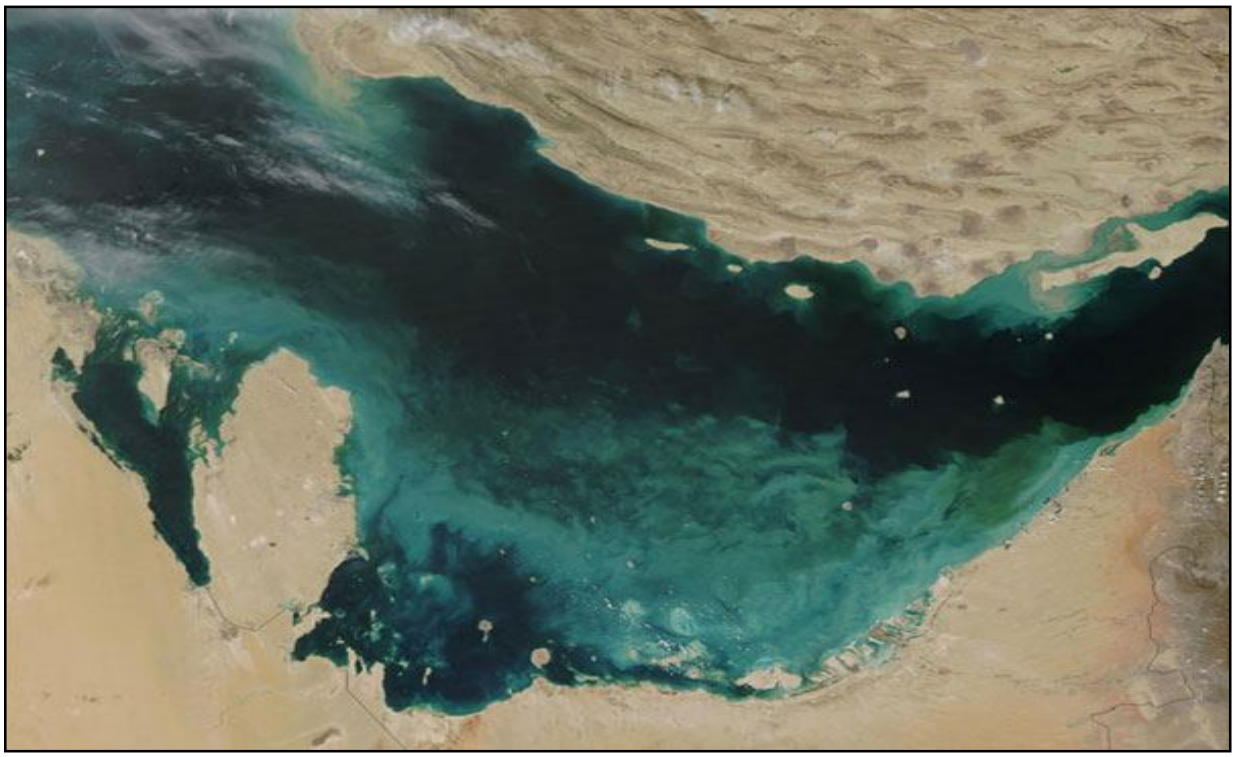


Figure 1.1 : White precipitate sightings in the Persian Gulf.

This interesting finding had become the main motivation for the study of formation of calcium carbonate from seawater under the effects of temperature variation.

Apart from that, the CO_2 content in the atmosphere has become a concern for us since it is increasing each year. According to Earthtrends, 2003, the total emission of CO_2 in Malaysia in year 1998 was recorded to be 120,475 thousand metric tons [2]. 54% of the total emissions come from liquid fuels sources, 30% from gaseous fuels, 6% from solid fuels and gas flaring and the rest 4% from cement manufacturing [Appendix 1.1]. In the other hand, Malaysia has raised the awareness of the present level of CO2 emission by being committed to the Kyoto Protocol under the United Nations Framework Convention on Climate Change (UNFCCC), and large number of companies that operates in Malaysia has started to join the protocol. According to Carbon Management Consulting Group, an international consultant on greenhouse gases and global warming, said that an estimated 1,500 Malaysian companies are expected to be certified by the year 2009 [3], based on the number of projects to be presented to the United Nation for validation approval.

Apart from that, $CaCO_3$ possessed high potential to generate profits. The statement is due to its high demands which mostly come from paper making industries and polyvinyl chloride (PVC) production industry. $CaCO_3$ is one of the main raw materials used in making high quality paper. In addition, it favorable to most paper making companies to use $CaCO_3$ as the main ingredients in paper making as an alternative to forestry as it raised too many issues concerning the environment. Apart from reducing the logging activity, $CaCO_3$ can also produces high quality paper compared to wood pulps.

Therefore, it is great to say that studying the natural sequestration of CO_2 in seawater and the effects of temperature upon it will great benefits us, since the knowledge can be applied to manipulate the temperature effects towards the formation of $CaCO_3$. In addition, it can also provide an alternative to naturally sequestrate CO_2 in seawater as to reduce the CO_2 impact towards the environment.

1.2 Problem Statement

Despite impact of CO_2 towards the environment, CO_2 actually serves well in the petroleum industry by being one of the major components in the Enhanced Oil Recovery (EOR) technology. Nowadays, EOR has become one of the important approaches of maximizing the natural gas recovery from the gas reservoir. The gas injection method is the most applicable method used in the process, mainly using CO_2 gas as the main source for the process. The EOR process via CO_2 can be observed from the step by step process provided in Figure 1.2 [4]. The CO_2 gas recovery process takes place from the separation and capture process from the flue gas of the power plant. The recovered CO_2 gas is then transported towards and injected into the oil reservoir. Until recently, most of the CO_2 used for the enhanced oil recovery has come from naturally-occurring reservoirs and power plants through further complicated CO_2 gas separation processes.

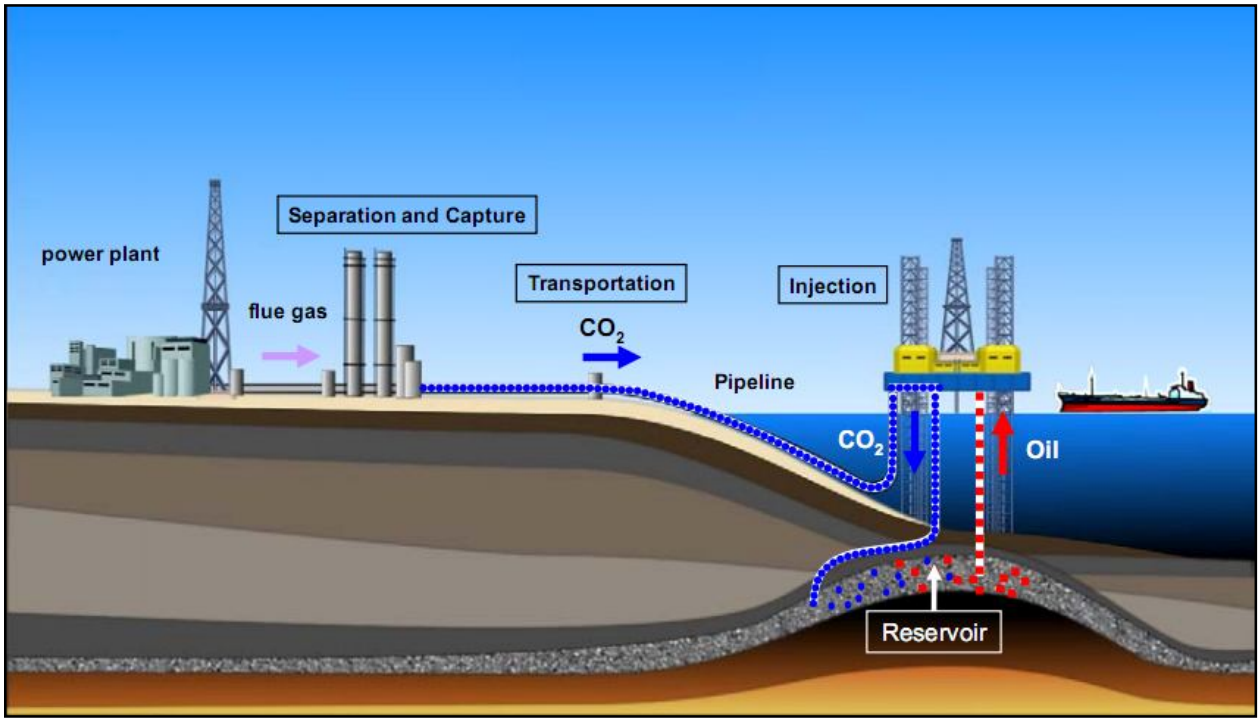


Figure 1.2 : Enhanced oil recovery process via CO_2 gas injection.

Question arises of what will happen to the trapped CO_2 inside the reservoir after the process is done, whether or not the CO_2 gas will remain inside the reservoir and sequestrate naturally inside seawater. This is one of our main interests that lead towards the study, as the study will focus on the natural sequestration of CO_2 gas inside seawater and how temperature affects it.

1.3 Objectives and Scope of Study

The main objective of the study is to the natural sequestration of CO_2 in seawater along with the effects of temperature variation towards the formation of calcite and aragonite in seawater. First and foremost, before beginning the study, sufficient knowledge which is related to the study must first be gained. Therefore, relevant literature reviews and researches are done and revised. The importance of the literature studies is to grasp the fundamental theories and recent studies that are related directly or indirectly so that we will be able to apply it during the study. Several literature papers concerning the effects of temperature towards formation of $CaCO_3$ formation we done. During the process, we came across several established studies that are related. All those papers and studies were carefully studied, screened and used as a guide throughout the study. In addition, from the literature, we also identified several other factors that have impacts towards formation of $CaCO_3$ that cannot be neglected such as the pH level of the seawater. By combining all the essential knowledge, then we can finally construct the experiments to study the relationship.

Apart from that, the study also requires some basic knowledge on constructing relevant experiments that will contributes to the study. Furthermore, the study clearly requires good analytical and characterization skills and sometimes with the aid of advanced laboratory equipments such as the X-Ray Diffraction (XRD) scanning and the Scanning Electron Microscope (SEM). With the help of the equipments, more details information can be gathered and then will finally lead towards more accurate and justified results. In addition, good justification and data interpretation skills are also required as to provide good arguments and discussion with regards to the study done.

1.4 Relevancies of Study

By studying the natural sequestration process of CO_2 along with the temperature effects towards the formation of $CaCO_3$ we can also study the possible ways to gain benefits from the high CO_2 content in the atmosphere, as we are all belief that CO_2 is one of the contributors of air pollution and ways to reduce it.

In addition, calcium carbonates have a great economic potential since its demands is high nowadays and the application is wide. Aragonite physically has harder physical crystal structure compared to calcite, making its more valuable.

Apart from pursuing the main objective of the study, it can also provide the exposure towards experimental and laboratory works, which requires adequate equipment and chemical handling skills.

CHAPTER 2

LITERATURE REVIEW

2.1 Formation of Calcium Carbonate from Seawater

The open sea that covers one third portion of the earth houses numerous species of microorganism and macro organism in it. Decayed sea inhabitant corpses, absorbed gases from the atmosphere and minerals from the land causes the contents of the seawater to be enriched with minerals. Under certain condition, carbonate ion that comes from the absorption from the CO_2 gas in the seawater will reacts with the calcium ion from the seawater itself to form calcium carbonate solid. The formation process of $CaCO_3$ in seawater can be briefly explained from the following chemical relation:

$$CO_2\,(g) + H_2O\,(l) \leftrightarrow H_2CO_3\,(aq)\ \text{(carbonic acid)} \qquad (1)$$

$$H_2CO_3\,(aq) \leftrightarrow H^+\,(aq) + HCO_3^-\,(aq)\ \text{(bicarbonate ion)} \qquad (2)$$

$$HCO_3^-\,(aq) \leftrightarrow H^+\,(aq) + CO_3^{-2}\,(aq)\ \text{(carbonate ion)} \qquad (3)$$

$$Ca^{+2}(aq) + 2HCO_3^-(aq) \leftrightarrow CaCO_3(s) + CO_2\,(g) + H_2O(l) \qquad (4)$$

As the calcium ion content is very limited in the seawater, mainly 1.18 % of the total salinity of the seawater, it becomes the limiting in the dynamic reaction factor in which the formation calcium carbonate will no longer occur once the carbonate ion is fully depleted. Table 2.1 lists the chemical ion contents in the seawater and proportions accordingly [5].

Table 2.1 : Chemical ion contents in the seawater and its proportions.

Chemical Ion Contributing to Seawater Salinity	**Concentration in o/oo (parts per thousand) in average seawater**	**Proportion of Total Salinity (regardless of salinity level)**
Chloride	19.345	55.03
Sodium	10.752	30.59
Sulfate	2.701	7.68
Magnesium	1.295	3.68
Calcium	**0.416**	**1.18**
Potassium	0.39	1.11
Bicarbonate	0.145	0.41
Bromide	0.066	0.19
Borate	0.027	0.08
Strontium	0.013	0.04
Fluoride	0.001	0.003
Other	less than 0.001	less than 0.001

2.2 Established Precipitation Method and Synthesis of Calcium Carbonate

The most common and cheap source of obtaining $CaCO_3$ is through precipitation process. Rather than GCC, PCC production is cheaper and environment friendly. It does not require abusive excavation at the hillsides. In fact, the amount of production can be controlled, making it a favorable alternative practiced by most $CaCO_3$ manufacturers. $CaCO_3$ can be manufactured artificially nowadays, through varies of methods. Some of the examples of available methods nowadays in $CaCO_3$ producing are the Kraft Pulping method, carbonation and mixing of solutions, as shown in Figure 2.1 [6]:

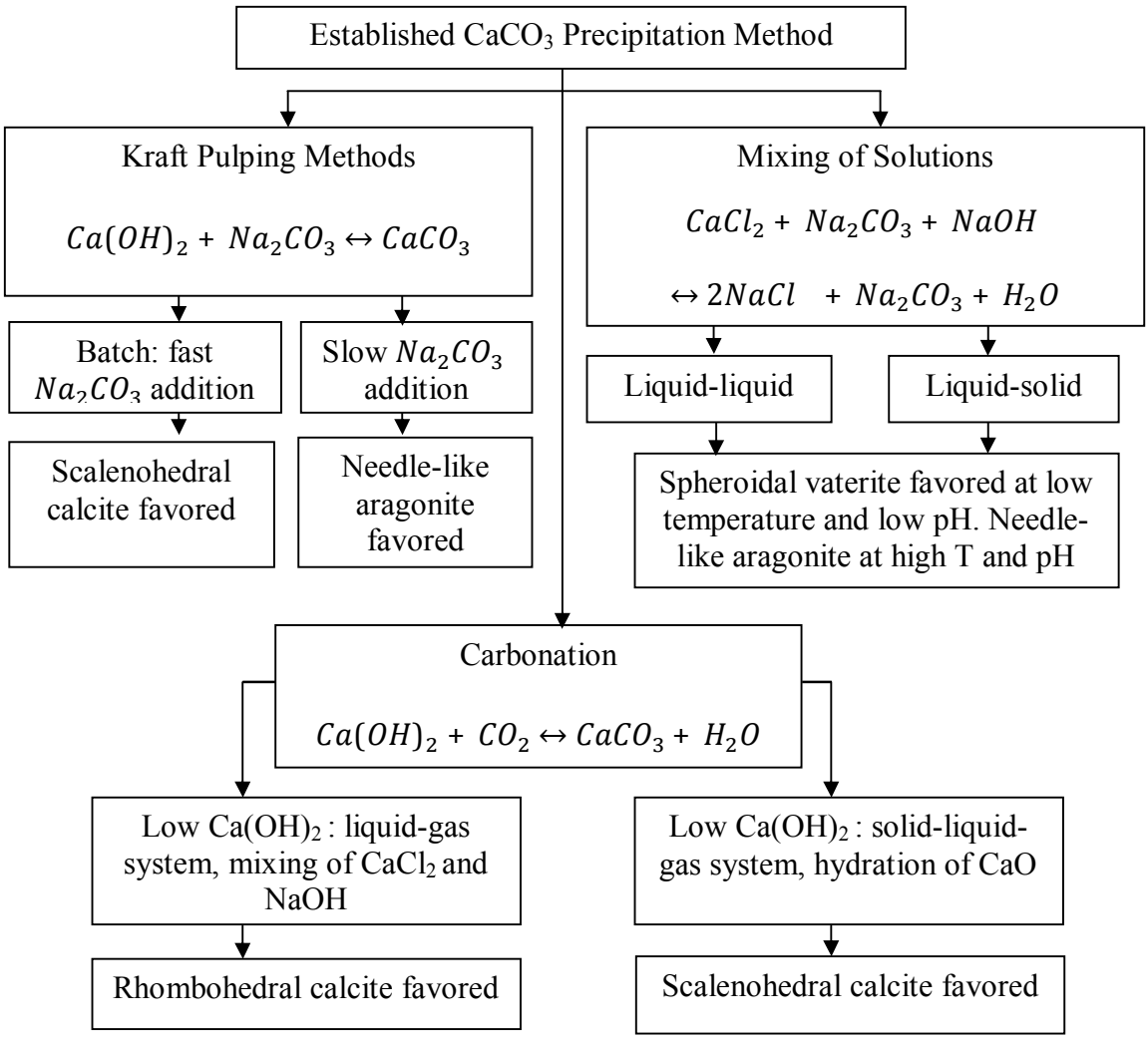


Figure 2.1 : Established Precipitation Methods

2.2.1 Kraft Pulping Method

This method was introduced by Ji-Whan Ahn et al. (2005). The procedures involve mixing of calcium hydroxide and sodium hydroxide in a tank with solution of sodium carbonate [7]. Furthermore, ripening process takes place, followed by filtering and drying of sample. Finally, characterization stage is done with the sample via analysis of results obtained via Scanning Electron Microscopy (SEM) analysis and X-ray Diffraction (XRD) analysis. Figure 2.2 explains the flow of Kraft Pulping Method.

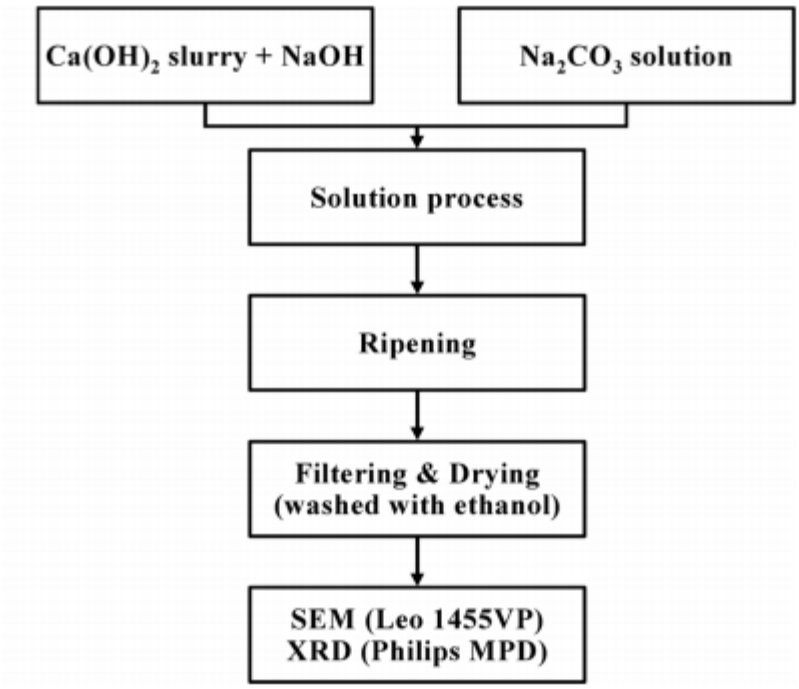


Figure 2.2 : Kraft Pulping Method

Super saturation relates directly with the formation behavior of PCC polymorphs, and super saturation in precipitation reaction depends on the ion concentration of the reactants present in the solution. The range of super saturation was adjusted to three different levels: high, medium and low.

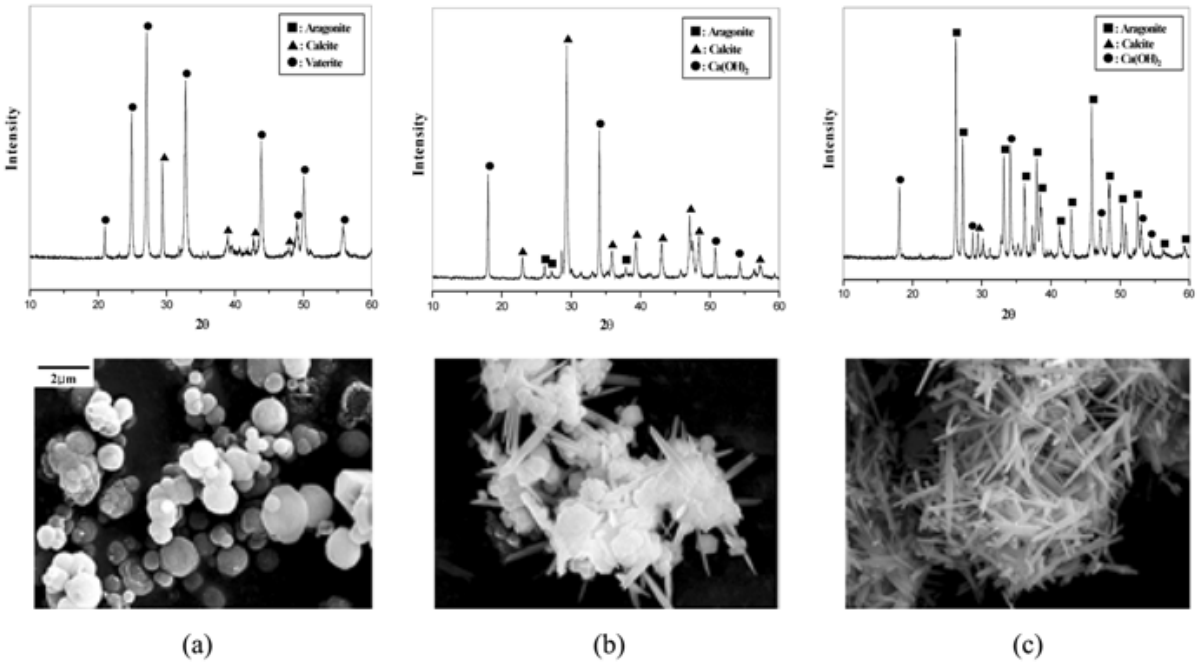


Figure 2.3 : XRD patterns and SEM images of PCC synthesized in three reaction system level; (a) High, (b) Medium and (c) Low

Formation properties of synthesized PCC in the three reaction systems are shown Figure 2.3. At high super saturation, the rate of crystal nucleation increases, while the size of the critical nuclei then became smaller [7]. Referring at Figure 2.3 (a), at high saturation level, vaterite mainly takes place and has the smallest particle size among PCC polymorphs and it has spherical shapes.

Figure 2.3 (b) shows the result for medium super saturation level. In this reaction, calcite was mainly formed with some mixed of aragonite crystal, while in Figure 2.3 (c), the results of the reaction at low super saturation level, with aragonite crystal dominates formation dominates over any other forms of $CaCO_3$ crystal formation.

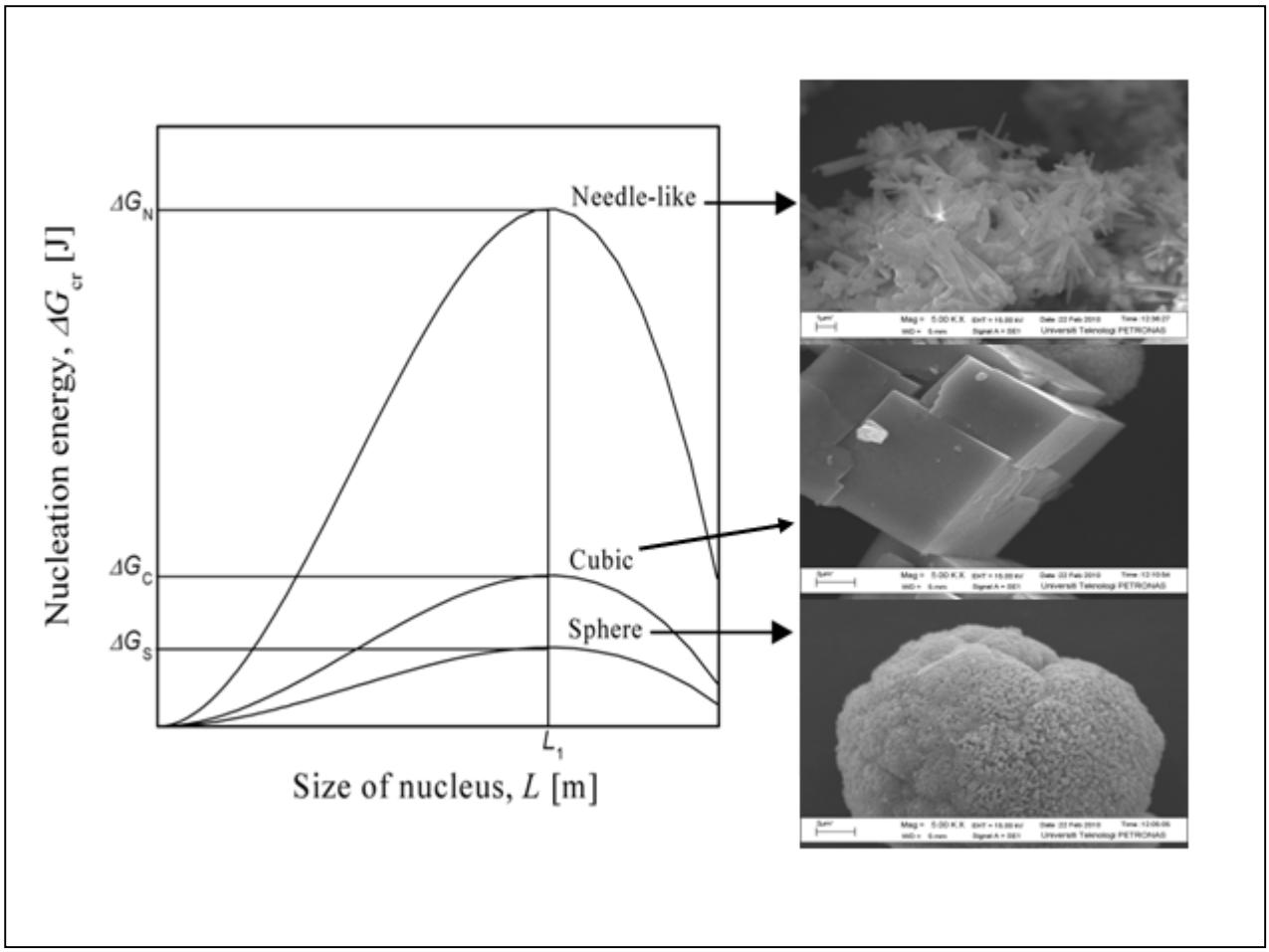


Figure 2.4: Critical free energy for nucleation having size of L_1 for the polymorphs of precipitated calcium carbonate in forms of needle-like (aragonite), cubic (calcite) and spherical (vaterite) [7].

2.2.2 Carbonation of calcium hydroxide

According to this method, PCC can be artificially formed from the carbonation process of calcium hydroxide. By injecting CO_2 inside the solution, $CaCO_3$ will precipitate taking form of calcite crystal.

2.3 Solubility of Carbon Dioxide in Seawater

Carbon dioxide does dissolve in water. However, the process is somewhat complex and will behave differently under different conditions. When it dissolves, it undergoes reactions to form four different carbonate species can be present; CO_2 (aqueous), H_2CO_3 (aqueous), HCO_3^- (aqueous) and CO_3^{2-} (aqueous). Modification of the simple Henry's law calculation is required in order to calculate the total solubility of carbon dioxide and individual concentrations of all carbonate species [8]. The process takes into account the influence of these reactions in calculating CO_2 gas solubility.

This study is based on the study done by Khalid Al-Anezi et al., 2006 to study the parameters affecting the solubility of carbon dioxide in distilled water, artificial seawater and actual seawater tested at different sets of temperature [8]. The experiment uses one liter of aqueous solution, purged with pure N_2, then 2% CO_2–98% N_2 gas mixture was introduced to the reaction vessel at a constant flow-rate of 150 mL/min and known pressure. The vapor flowing out of the reaction vessel was split into two stream flows, the main outlet vapor flow via a ChromPack Gas-Clean Moisture Filter and gas flow-meter at flow-rate of 40 mL/min and the second vapor flow was vented. The main outlet vapor was analyzed continuously to measure the amount of CO_2 gas in the outlet vapor line by the CM-5011 Carbon Coulometer.

Once equilibrium has been reached the, experiment is stopped. The data collected and then the solubility of CO_2 in solution and Henry's law constant will be calculated. The experiment is completed, and the calculation process yields the following results, as shown in Figure 2.5. From the result, we can observe that the solubility of CO_2 in the three solutions decreases as the temperature increases. During the process of measuring the solubility of CO_2 in different aqueous solution it was found that the presence of different salts in the solutions would reduce the CO_2 gas solubility in the solutions.

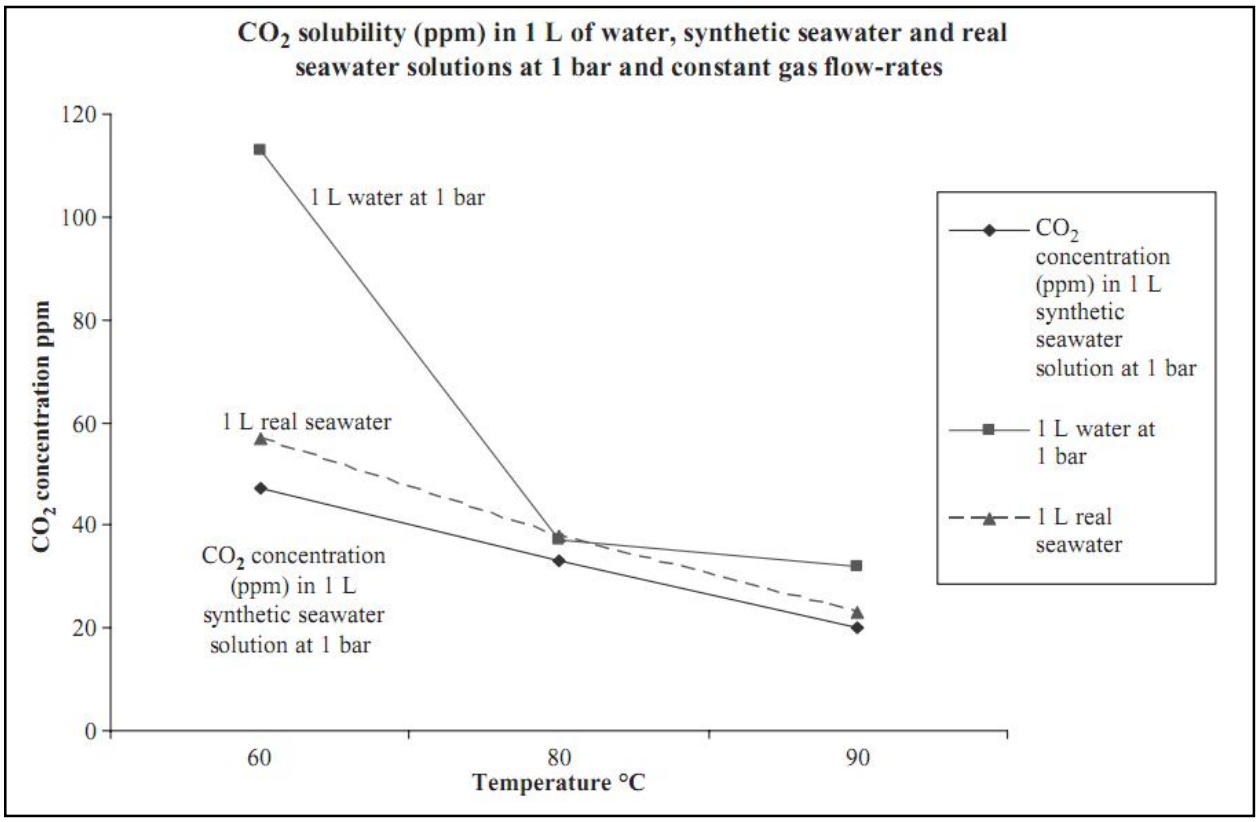


Figure 2.5: CO_2 solubility (ppm) in 1 liter of water, synthetic seawater and real seawater solutions at 1 bar and constant gas flow-rates.

2.4 Alkalinity Effects on Carbon Dioxide Solubility in Seawater

The existing natural condition of seawater, in terms of pH cannot promote the formation of calcium carbonate even with an abundant supply of pure carbon dioxide gas. This is because the carbon dioxide molecules must dissolve into carbonate ions first in order for the calcium ion to capture it to form calcium carbonate ion. However, there was an argument in this case whether it is possible for natural state of CO_2 to be synthesized into the carbonate ion, due to facts that double bond binds the molecular structure of the gas. Despite the arguments, there is an approach done by Keith E. Chave and Erwin Suess [9], proving that upon reaching mild alkaline condition, approximately at pH 9.5, $CaCO_3$ formation can proceeds, proving that carbonate ion exists in the indicated mild alkaline condition

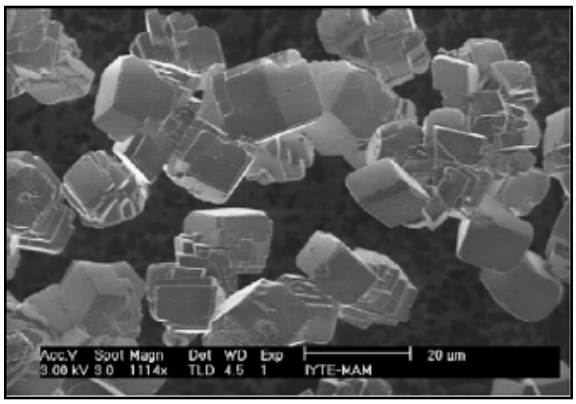
2.5 Effects of Temperature Variation on Formation and Morphology of Calcium Carbonate

According to E.Altay, T.sahwan and M Tanoglu, (2006), crystal morphosynthesis of $CaCO_3$ will be greatly affected by the temperature variation [10]. Experiment is done by using aqueous mixture of 0.05 M sodium carbonate mixed with 0.05 M calcium chloride. The pH of the solution was adjusted to pH 9.0 to provide mild alkalinity condition. Furthermore, the aging time of the mixture was extended to relatively from 30 minutes to 1 week. The selected temperatures for the experiments were 20°C, 30°C, 40°C, 50°C, 60°C, 70°C, 80°C and 90°C. The experiment was expected to have the results of different crystal morph at each different temperature.

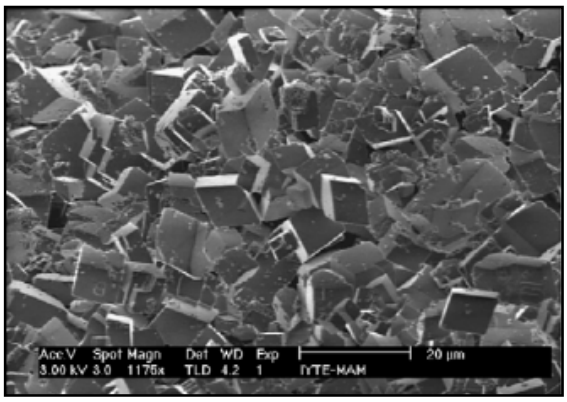
As the results of the experiment, precipitation of $CaCO_3$ was achieved at all tested temperature, however, forming different pattern of crystal morph at different range of temperature. Figure 2.6 shows the results obtained from the experiment through SEM analysis [10]

Referring to Figure 2.6, different patterns of crystal morphs were formed at each different temperature. At temperature 20°C, rhombohedra-structured crystals (calcite) can be observed from the SEM images. The crystals formed fit the characteristics of calcite type of $CaCO_3$. However, at higher temperature of 50°C, a mixture of rhombohedra-structured crystal can be observed along with the existence of a few orthorhombic-shaped crystals (aragonite). These was further determined as a mixture of calcite and aragonite crystal. Apart from that, at temperature of 80°C, only orthorhombic-shaped crystals can be observed. Significantly, aragonite crystal dominates over formation of any other form of calcium carbonate.

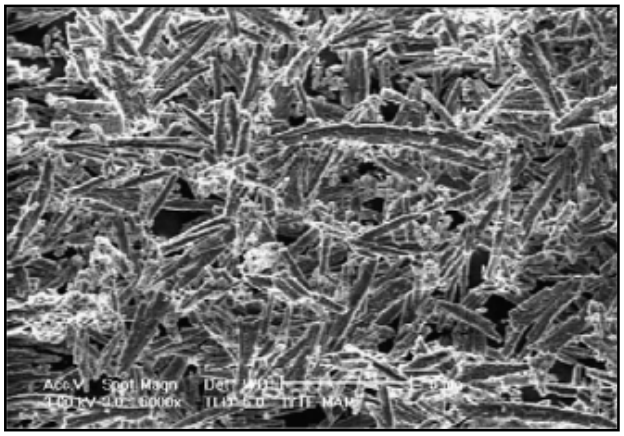
This significant study would provide an important reference towards the study of precipitation of $CaCO_3$ as we can classify types of crystals formed further whether the crystals formed are aragonite or calcite.



(a)



(b)



(c)

Figure 2.6 : SEM images of $CaCO_3$ crystals prepared at mixing temperature of (a) 20°C, (b) 50°C and (c) 80°C

2.6 Effects of Concentration Variation on Formation of Calcium Carbonate

In different perspective, a study was done by John W. Morse, Rolf S. Arvidson, and Andreas Luttge, (2007) to study the effect concentration variation towards the nucleation pattern of calcium carbonate from seawater. The study indicates that the variation of nucleation is caused by the magnesium calcium ratio inside the seawater. At lower magnesium calcium ratio, the nucleation of calcite is favored. However, as the temperature increases, the nucleation tends to favor to forms more aragonite. At higher magnesium calcium ratio condition, aragonite forms faster as the temperature raises, compared with the aragonite formation at lower magnesium calcium ratio [11].

The relationship of magnesium calcium ratio on the nucleation of calcite and aragonite at different temperature can be simplified into Figure 2.7.

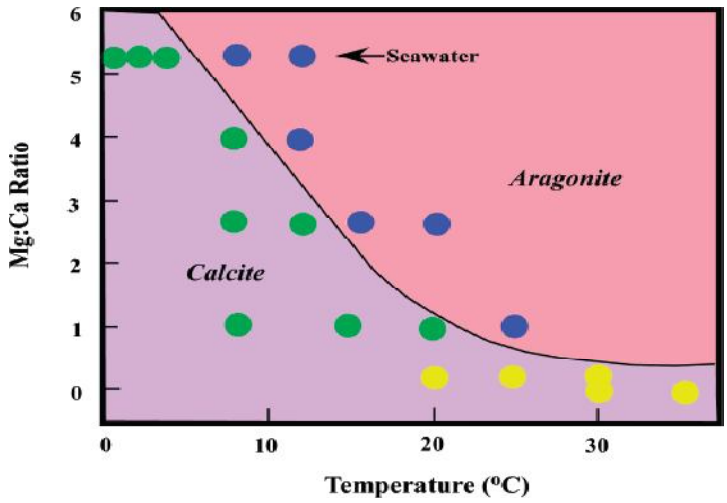


Figure 2.7 : Relationship of Influence of Mg/Ca ratio towards the nucleation of calcium carbonate in forms of aragonite and calcite

By referring from the results obtained in Figure 2.7, in can be concluded that at high Mg:Ca ratio, the crystallization of $CaCO_3$ is favored by aragonite rather than calcite upon moving towards high temperature. However, at low Mg:Ca ratio, calcite is more favorable at lower temperature, then aragonite as the temperature raises. By observing the relationship, we can use the information to compare it with the study.

Conclusively, apart from temperature, there are other factors that might have effects on the formation of $CaCO_3$ from seawater. However, this study will only focus on the temperature effects towards the formation process.

CHAPTER 3

METHODOLOGY

From the previously done literature reviews, we had pinpointed some of the important keys to investigate the effects of temperature towards the formation of calcium carbonate from seawater. For the experiment part, we divided it into two main sections of the study. The first section is to investigate the relationship of temperature variation towards the formation of calcium carbonate by using artificial seawater as the main solution while the second section is to investigate the relationship of temperature variation towards the formation of calcium carbonate by using actual seawater as the main solution.

For the first part, the artificial seawater is consisted of mixture of 0.05M Na_2CO_3 and 0.05M $CaCl_2$. The importance of using the artificial seawater is that we can actually manipulate the concentration of calcium inside the solution by varying the concentration of the $CaCl_2$ inside the solution by mixing it at different mole of solution. The solution will only contain the respective ions that will combine to forms $CaCO_3$ without any presence of additional ions when injected with pure CO_2 gas. This preliminary experiment basically tests out the basic theory of formation of $CaCO_3$ chemically. Furthermore, the results of the experiment will be characterized and compared with the literature reviews. This process was done with the help of the XRD and SEM analysis, to confirm whether or not the results of the experiment will be $CaCO_3$. The XRD analyze the contents of the products of the experiment in solid form and class it according to elements that presented in the product with its respective intensity. In other words, the XRD analysis will confirm the presence of aragonite and calcite in the product and shows the pattern of formation of each, respectively. In the other hand, the SEM analysis with focuses on the physical structure of the product formed in microscopic level. The size of the particle can also be studied by adjusting the magnification level in accordance to its size. Apart from the size, the most important aspect that needs to be studied is the physical structure of the product. Again, by comparing the physical structure of the product (in forms of fine crystal), we can differentiate whether the

product formed is consisted of aragonite or calcite. It can also be other elements that formed during the process, thus the analysis is crucial towards the outcome of the study.

For the second part of the experiment, actual seawater will be used as the solution that will be injected in with pure CO_2 gas. The same goes to this experiment where temperature will be the manipulated variable and as what had discovered in the literature reviews earlier, the pH level of the seawater will be maintained at basic level of pH 10.5 in order for the reaction to take place. The next step of the experiment is about the same as the first part where characterization process will be done using the same method. Figure 3.1 summarizes the methodology of the experiments.

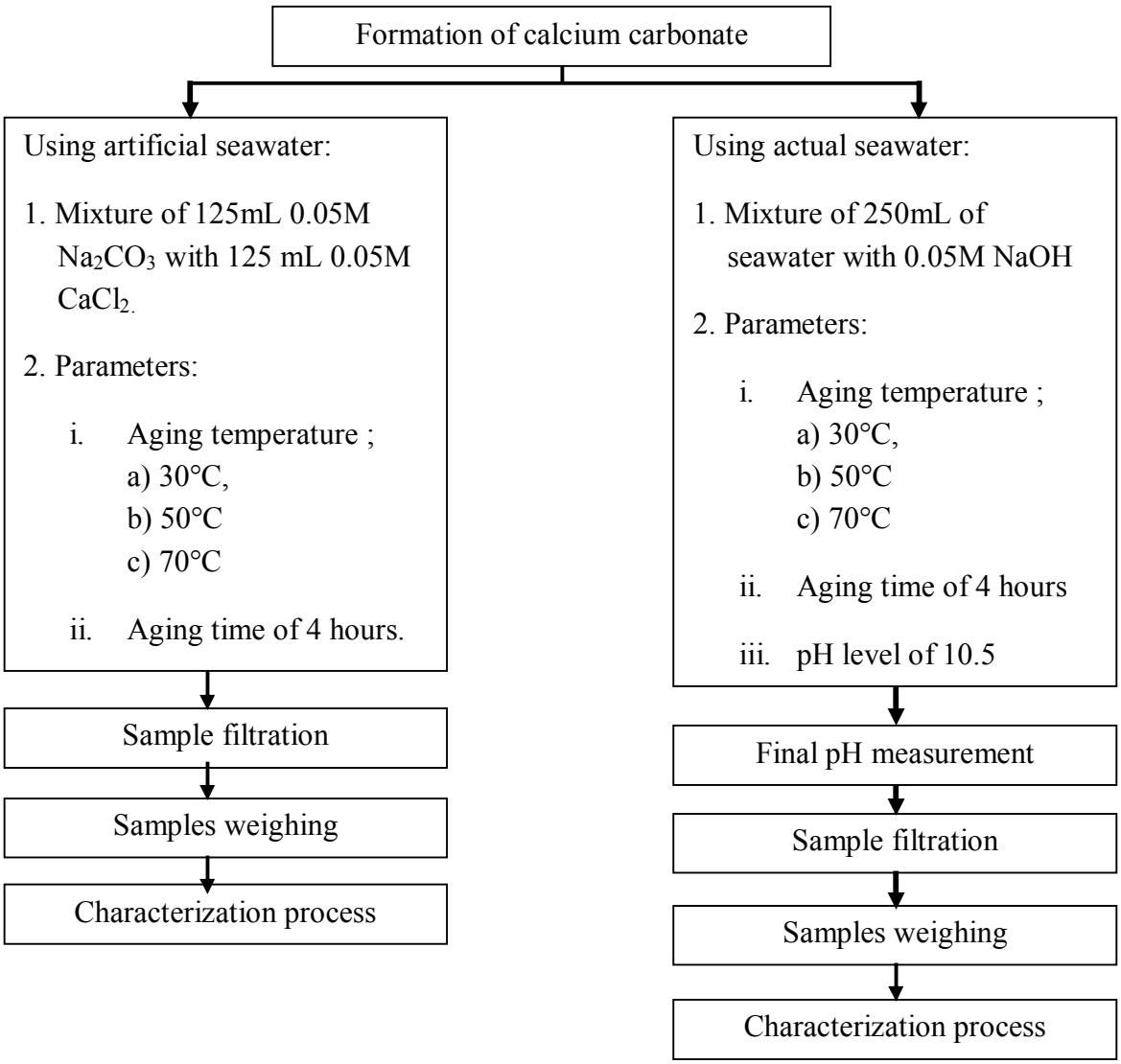


Figure 3.1: Methodology of the experiment

3.1 Formation of $CaCO_3$ from artificial seawater

In the experiment, the preparation of stock 0.05M Na_2CO_3 mixed with 0.05M $CaCl_2$ is first prepared. The mixture was then distributed equally into three flasks at 250mL each. The motive of doing so is that all three flasks will have similar mixture of compound and expected to exhibit certain results in the further temperature testing. All the three flasks will undergone three different aging temperature of 30°C (ambient), 50°C and 70°C each. The temperature is kept constant at respective temperature by putting all three flasks in a different water bath at respective aging temperature. After that, pure CO_2 will be injected into the flasks through a tube, connected to the gas regulator and the CO_2 supply. The gas will bubble up in the solution at constant rate. This experimental setup can be observed from Figure 3.2. The bubble is controlled to flow as small as possible in order to maximize the contacts will the mixture. The water bath will be left for four hours aging time and then switched off when the time ended.

After it reached the aging time, the samples were taken out of the water bath and let to be cooled a bit. After the samples cooled off, the samples will be filtered by using a filter paper. Wet filtered samples are then let to dry off. After the sample had fully dried, the sample is weighted using the weighing scale. The weight of the samples is then recorded to observe the quantity of calcium carbonate formed inside each flask.

Finally, the characterization process with XRD and SEM analysis is done onto the samples to study the characteristics of the samples after the process finished. XRD analysis will analyze the contents of the samples and shows the pattern of the intensity of each substance formed respectively. Meanwhile, the physical structure can be observed from the SEM analysis later on. Both of the tests are crucial as to precisely determine whether the component formed is consisting of aragonite of calcite.

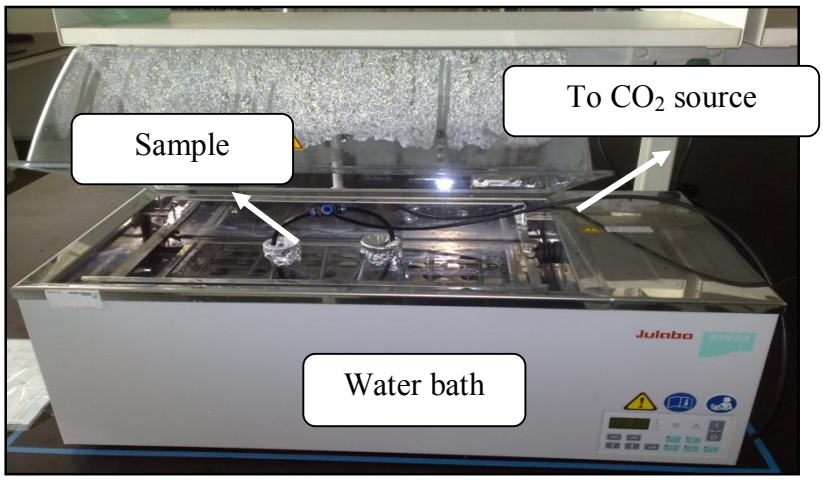


Figure 3.2: Experimental setup

3.2 Formation of $CaCO_3$ from actual seawater

Differ from the theoretical study done in the previous part, seawater is used as the main solution. 250mL of seawater is prepared in three flasks. Note that from the literature review, it is important for the solution to exist in mild alkaline state or else the reaction will not take place in order to do so, a few drops of 0.05M NaOH is dropped inside the flasks containing the seawater until the pH level of the mixture reaches pH 10.5. To make sure each samples are prepared at pH level of 10.5, the pH level of the samples are measured each time the drops mixed with the solution. This procedure is important to make sure that the pH level of the samples from deviating too far from the desired pH level. After the desired pH level is reached, the flasks were positioned at three different aging temperatures of 30°C, 50°C and 70°C inside a water bath. CO_2 gas was injected into the flasks, same as the previous experiment setup. The process is kept running for four hours aging time.

After it reached the aging time, the samples were taken out of the water bath and let to be cooled a bit. The final pH level of each samples were then measured to observe the difference in pH level of before and after of each samples. Next, the samples will be filtered by using a filter paper. Wet filtered samples are then let to dry off. After the sample had fully dried, the sample is weighted using the weighing scale. The weight of the samples is then recorded to observe the quantity of calcium carbonate formed inside each flask.

Finally, the characterization process with XRD and SEM analysis is done onto the samples to study the characteristics of the samples after the process finished, same as the previous part. XRD analysis will analyze the contents of the samples and shows the pattern of the intensity of each substance formed respectively. Meanwhile, the physical structure can be observed from the SEM analysis later on. Both of the tests are crucial as to precisely determine whether the component formed is consisting of aragonite of calcite.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Formation of $CaCO_3$ from artificial seawater

Under the experiment conditions set earlier, the results obtained will be briefly described. White precipitates can be seen formed in each flask. From the observation made, the white precipitates that formed in each flask appear to be at different physical and quantity as in Figure 4.1.

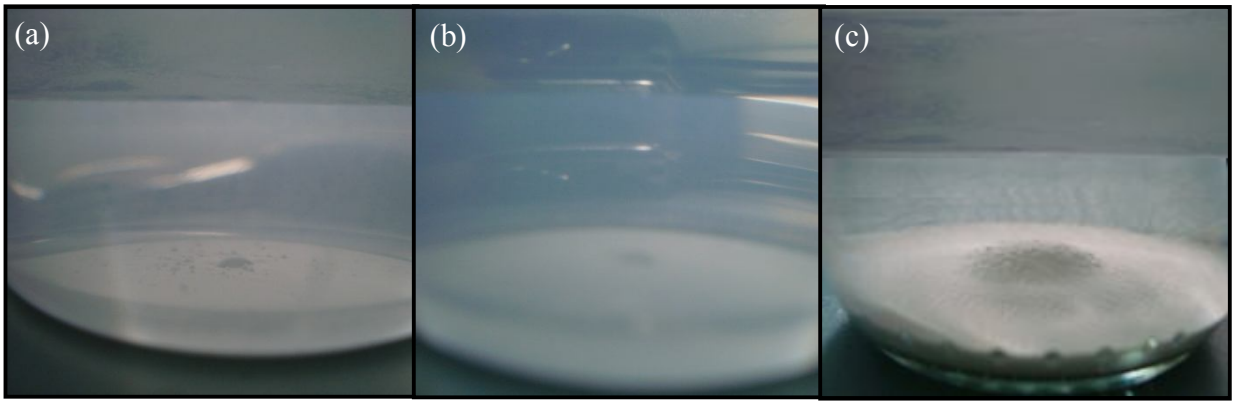
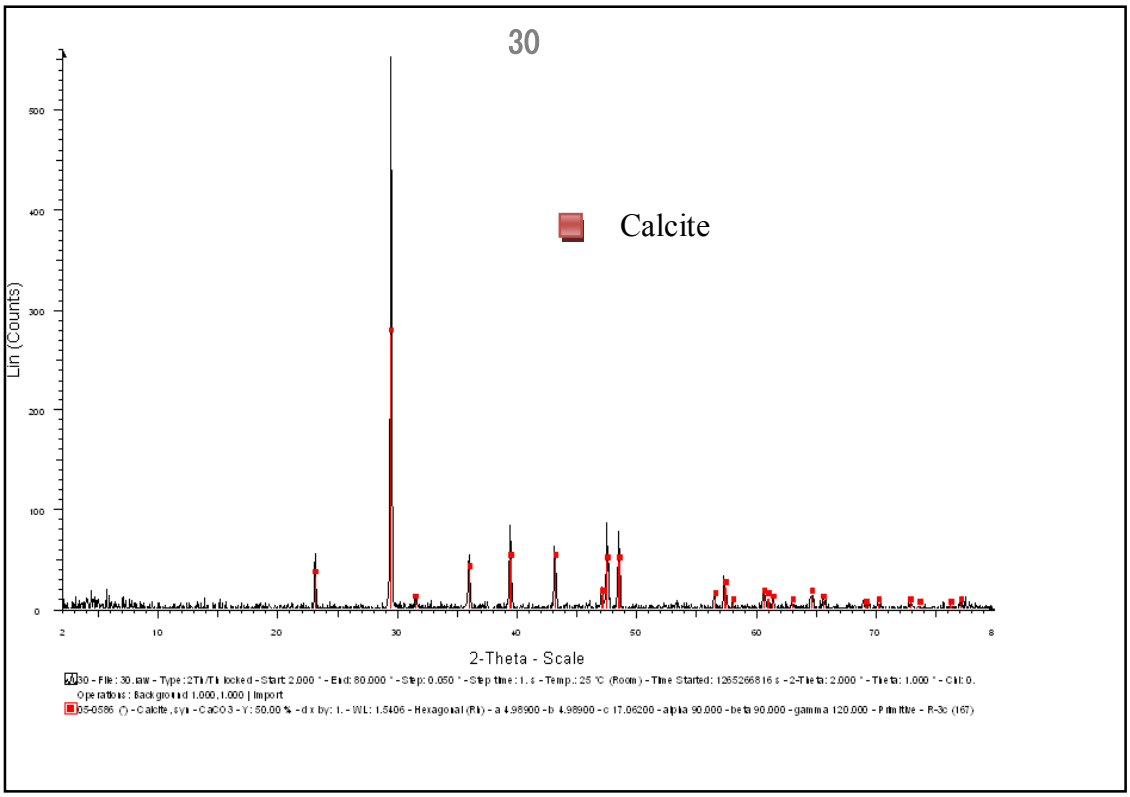


Figure 4.1: Formation of $CaCO_3$ at three different temperatures; (a) 30°C, (b) 50°C and (c) 70°C.

In beaker 'a' (Figure 4.1 (a)) and 'b' (Figure 4.1 (b)), fine precipitates formed in small amount at the bottom of the flask. Although the amount was very small, it is still recoverable after the filtration done with filter paper. In the meantime, large amount of coarse precipitates formed at the bottom of flask 'c' (Figure 4.1 (c)). The rate of formation of the white precipitates appears to be highest inside the 70°C sample. The sample was then filtered and measured after the samples completely dried up. Table 4.1 summarizes the precipitates formed inside the flasks. The precipitates formed in all flasks are expected to be $CaCO_3$. However, it can be further confirmed with the XRD and SEM results. The samples were sent to the lab for XRD and SEM analysis, and the results are as shown in Figure 4.2 (a), Figure 4.2 (b) and Figure 4.2 (c).



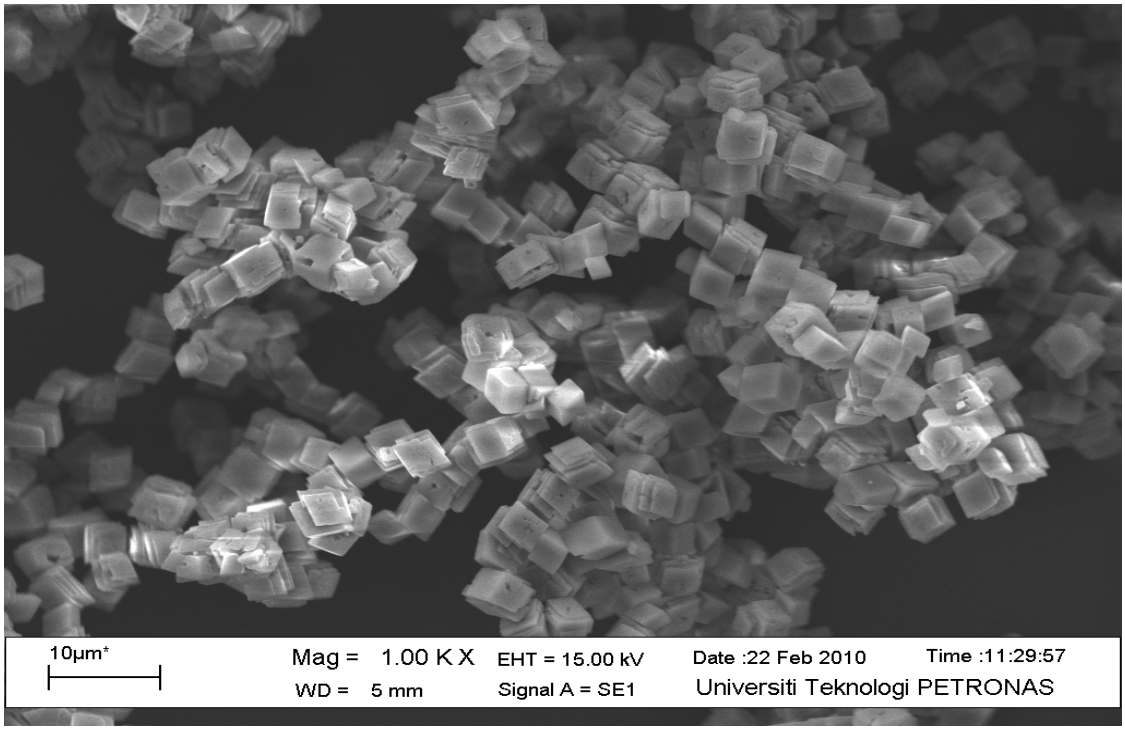


Figure 4.2 (a): XRD and SEM analysis at 30°C

Sample	Mass of $CaCO_3$ Formed (g)
T30	2.12
T50	2.32
T70	4.42

Table 4.1: Mass of calcium carbonate formed in each sample

Figure 4.2 (a) shows the results of XRD and SEM scanning of the sample run at 30°C. In the XRD result, it can be observed that calcium carbonate was formed inside the flask in form of calcite. Calcite exhibits the highest intensity inside the sample, as marked with the red line in the XRD graph. Apart from that, none other elements are traced in the sample. However, we cannot actually crossed out the fact that there are possibility that aragonite may existed inside the sample along with any other elements, since there are some other peaks beside calcite, however in smaller intensity. Since calcite possessed the highest and visible results it is best to conclude that only calcite was formed at 30°C.

In addition, the crystal structure of the sample can be observed in the SEM analysis. From the analysis, cuboid shape particle was formed. There is none other external particle was formed inside the sample. From the physical structure of the precipitate, we can identify the precipitate as having the physical features and shape of a calcite. The sizes of the crystals are evenly distributed one to each another. As mentioned in Table 4.1, the amount of calcium carbonate formed was very small, approximately 2.12 g in mass.

As discovered earlier in the literature, it is stated that at lower temperature of 30°C, calcite will formed inside the precipitation. By comparing the results obtained, it actually parallel with the one in the literature. Thus, we can say that the results obtained satisfy and confirmed that calcite was formed at lower temperature.

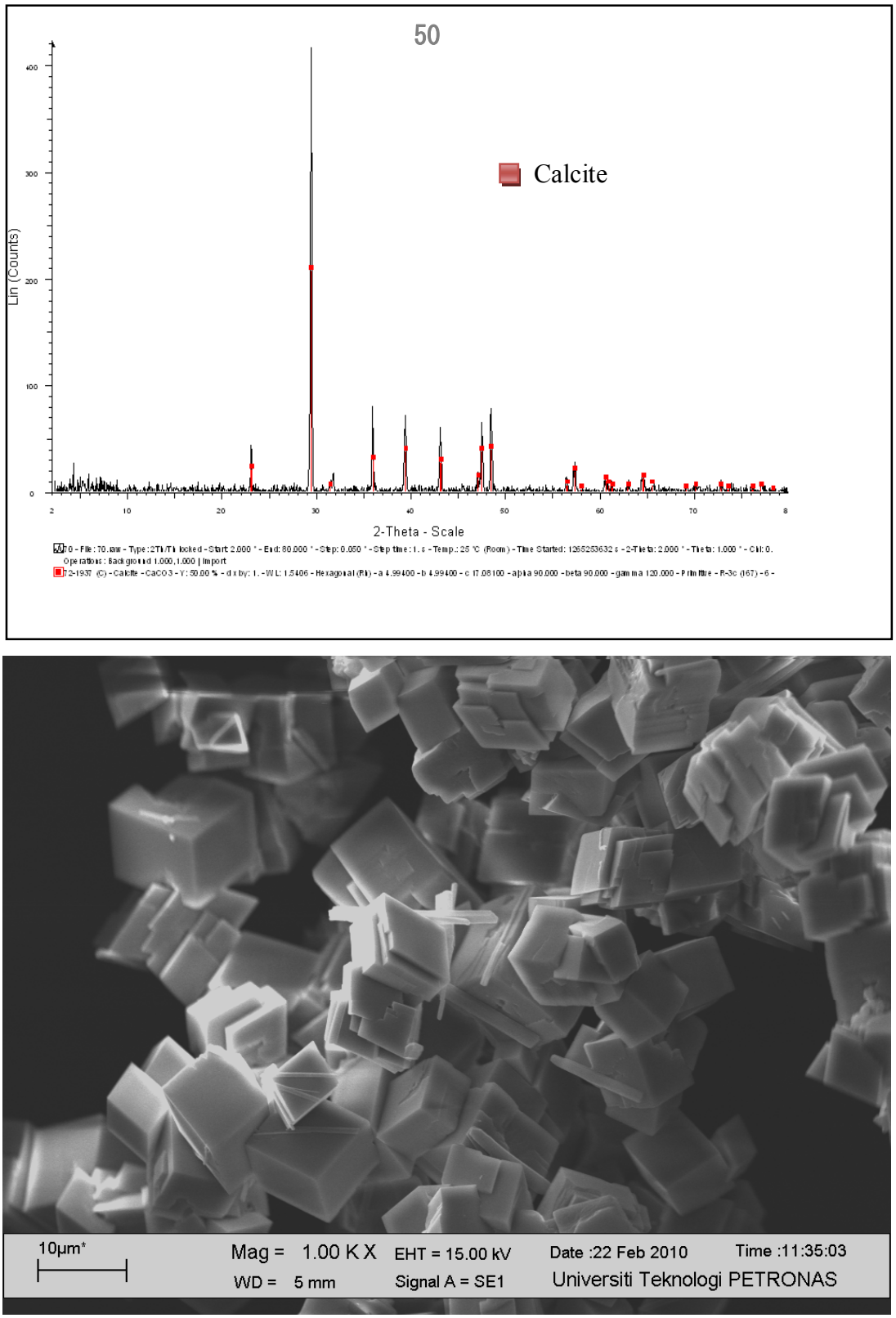
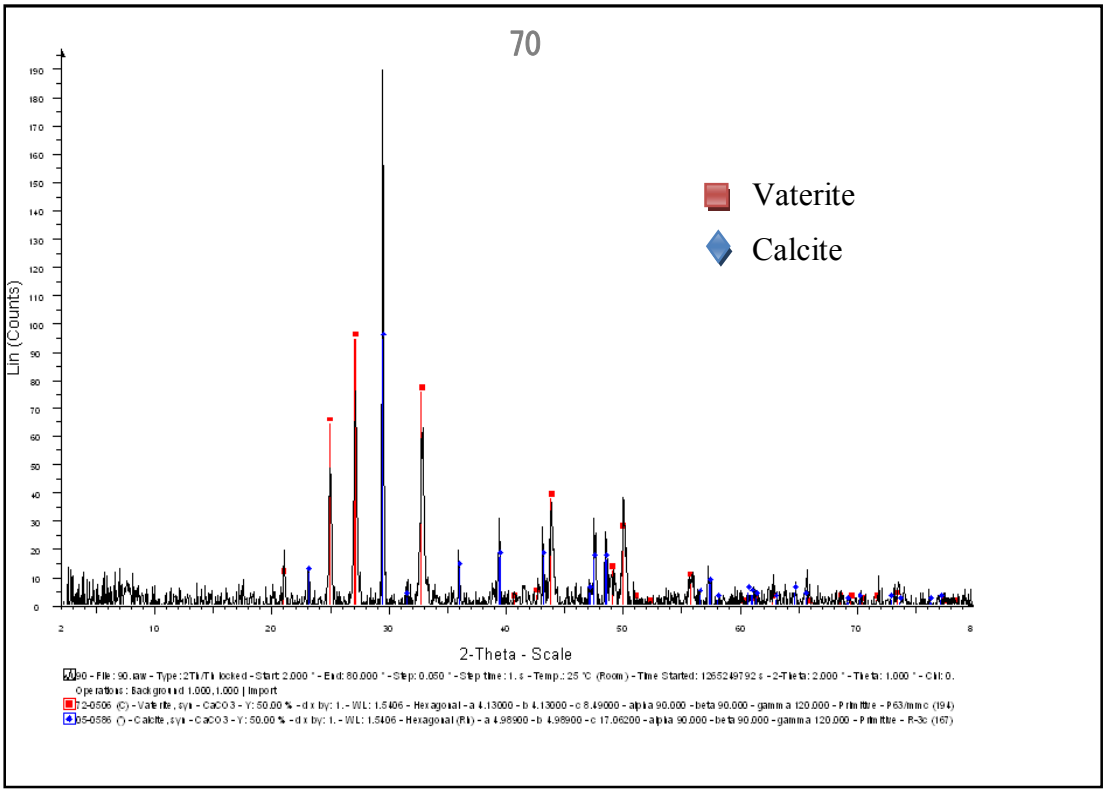


Figure 4.2 (b): XRD and SEM analysis at 50°C

Figure 4.2 (b) shows the results of XRD and SEM scanning of the sample run at 50°C. In the XRD result, it can be observed that calcium carbonate was formed inside the flask in form of calcite. Calcite exhibits the highest intensity inside the sample, as marked with the red line in the XRD graph. Comparatively, the result seems to be similar with the one obtained in part (a). Apart from that, none other elements are traced in the sample. However, as mentioned in the previous analysis, we cannot actually crossed out the fact that there are possibility that aragonite may existed inside the sample along with any other elements, since there are some other peaks beside calcite, however in smaller intensity. Similarly, since calcite possessed the highest and visible results it is best to conclude that only calcite was formed at 50°C.

Furthermore, the crystal structure of the sample can be observed in the SEM analysis. From the analysis, cuboid shape particle was formed, same as the previous result. However, closer looks of the picture shows that other than cuboid structure particles, there are small percentage of particle that formed in the same sample, having a needle-like structure. Referring to the literature, the needle-like structure of the crystal formed satisfies the characteristics of an aragonite. The rest of the cuboid shaped crystals are identified as calcite. The sizes of the crystals are evenly distributed one to each another. As mentioned in Table 4.1, the amount of calcium carbonate formed was very small, approximately 2.32 g in mass.

As discovered earlier in the literature, it is stated that at lower temperature of 50°C, calcite will formed inside the precipitation. By comparing the results obtained, it might be plausible those aragonites are also presence in the sample in the SEM scanning, but not in the XRD analysis.



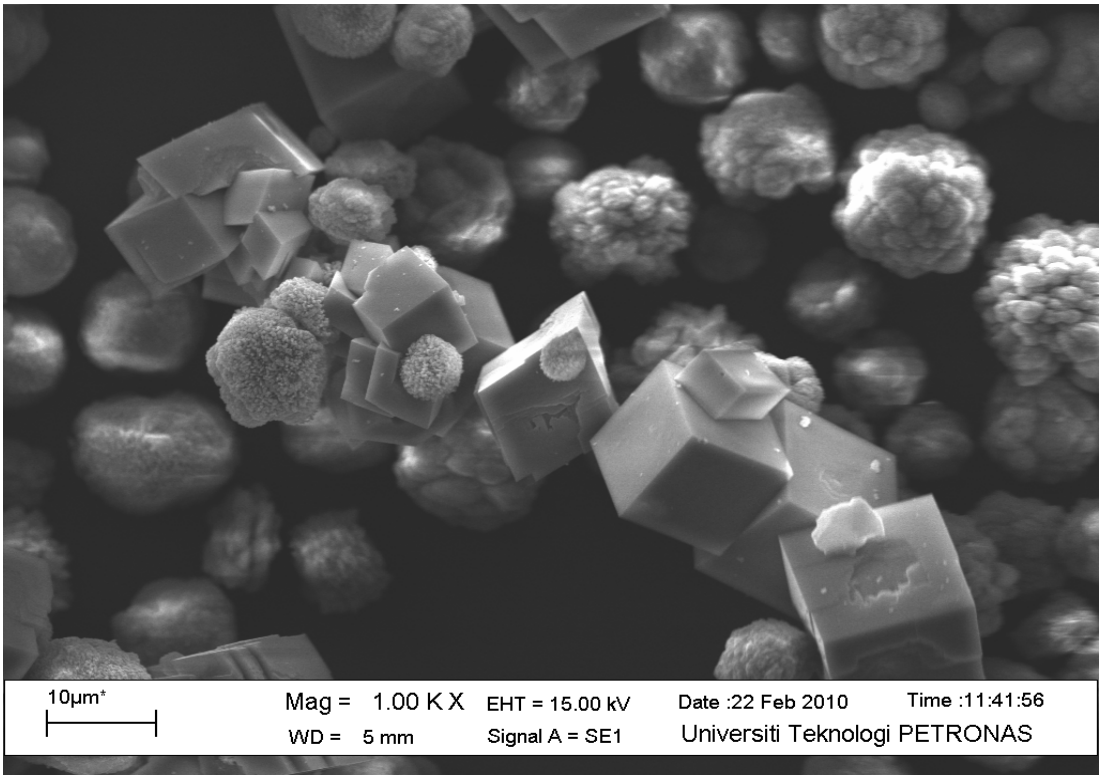


Figure 4.2 (c): XRD and SEM analysis at 70°C

Figure 4.2 (c) shows the results of XRD and SEM scanning of the sample run at 70°C. Surprisingly, calcite was not the only element present in the sample. Another form of calcium carbonate family, vaterite was traced to be the major precipitate that formed in the sample. From the SEM image, we can compare it with the XRD graph that the spherical shaped precipitate can be identified as vaterite. This is an interesting finding as from the literature reviews done, it was stated that vaterite can only exists in low nucleation energy condition. It is a possibility that vaterite was also formed not according to the nucleation energy factor, but also affected by the condition of the solution, say that the presence of external ions apart from calcium ion might disrupt the formation of calcium carbonate at higher temperature. The sizes of the cuboids and the sphericals are not evenly distributed, as shown in the SEM scanning. As mentioned in Table 4.1, the amount of calcium carbonate formed was higher compared with the previous two samples, approximately 4.42 g in mass.

Thus, we can conclude that based on the results obtained, at 30°C and 50°C, only calcite was present and at 70°C, both vaterite and calcite were present in the sample.

4.1 Formation of $CaCO_3$ from artificial seawater

From observations made in this experiment, white precipitates also formed inside the flasks for all samples that undergone different temperature conditions. The results of the XRD scanning and SEM images can be observed in Figure 4.3. Table 4.2 summarizes the pH changes of the samples, before and after the experiment finished.

However, the amount of the precipitate that formed in all samples was generally very much little compared with the one formed from the mixture of 0.05M Na_2CO_3 and 0.05M $CaCl_2$. This is due to due to the fact that the actual calcium content inside the seawater is too little, that is about 1.18% in percentage of the total contents. In this solution, calcium ion becomes the limiting factor of the formation of calcium carbonate. The amount of calcium carbonate formed will not increases furthermore once the calcium ion inside the seawater solution had been completely depleted.

Table 4.2: Temperature variation effect towards formation of $CaCO_3$ and pH level.

Sample	Initial pH	Final pH	Mass of $CaCO_3$ Formed
T30	12.20	6.4	1.46
T50	12.18	6.85	1.85
T70	12.13	7.2	2.1

The final pH seems to be related with the mass of $CaCO_3$ formed in each sample. The carbon dioxide gas dissolved inside the solution causes the acidity to increases significantly. The formation of calcium carbonate will use up the carbonate ion, thus decreasing the acidity of the solution. As can be observed in Table 4.2, the final pH of the sample T70 seems to be more basic compared with the other samples. However, the $CaCO_3$ formed is recorded to be the highest in mass. The reason is because the rate of formation of $CaCO_3$ is slightly higher at temperature 70°C, provided that the activation energy is slightly higher compared at lower temperature.

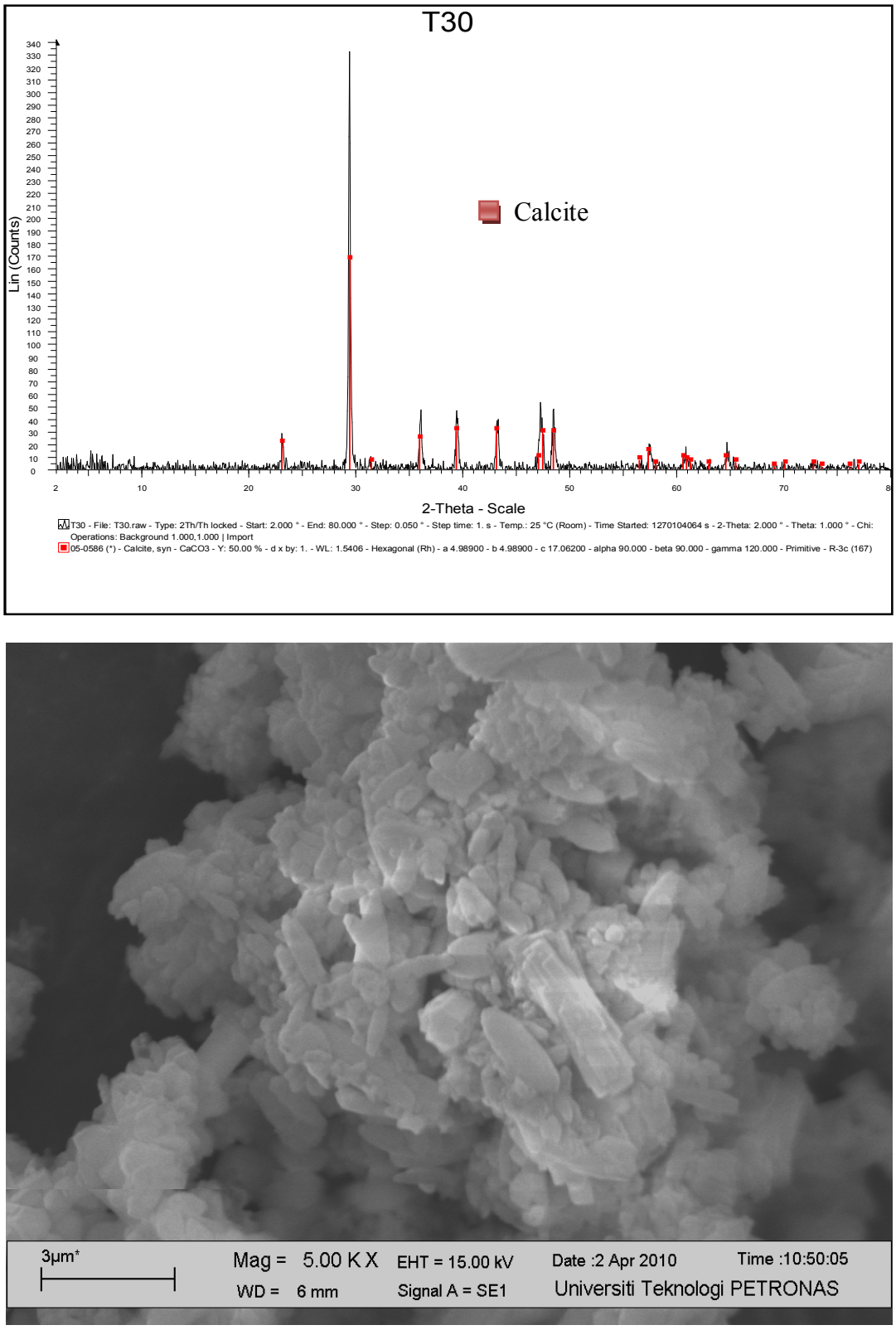


Figure 4.3 (a): XRD and SEM analysis at 30°C

Figure 4.3 (a) shows the results of XRD and SEM scanning of the sample run at 30°C. As expected, the XRD result shows that calcium carbonate was formed inside the flask in form of calcite. Calcite exhibits the highest intensity inside the sample, as marked with the red line in the XRD graph. None other elements are traced in the sample. However, referring to the SEM image, the shape of the precipitate formed was not exactly in cuboid shape, compared with the previous results of the same temperature. The calcite formed has a bulky cylindrical shape, or more like a deformed cuboid shape. Despite the inconsistency in shape, it can still be confirmed that the precipitate formed to be calcite, by referring to the XRD analysis.

In addition, the level of the pH of the solution seems to be dropping drastically at the end of the process. The explanation is that carbon dioxide actually dissolved in the seawater. As the carbon dioxide is acidic, it lowers the alkalinity of the solution towards more acidic solution.

Furthermore, the amount of calcium carbonate formed inside the sample is comparatively lower compared with the previous experiment, approximately 1.46 g only. This is due to due to the fact that the actual calcium content inside the seawater is too little, that is about 1.18% in percentage of the total contents, as mentioned earlier.

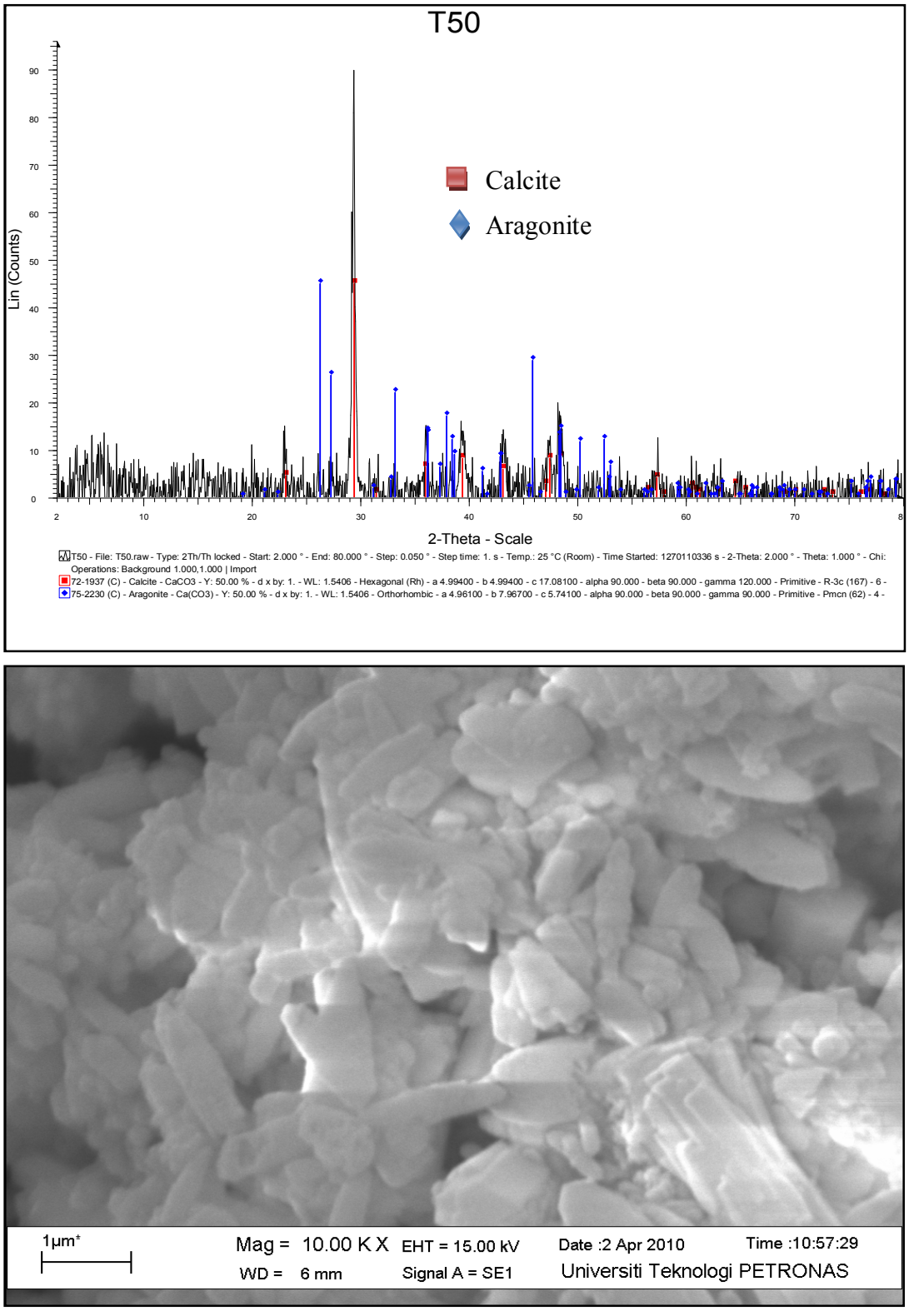


Figure 4.3 (b): XRD and SEM analysis at 50°C

Figure 4.3 (b) shows the results of XRD and SEM scanning of the sample run at 50°C. The XRD result shows that calcium carbonate was formed inside the flask in form of both aragonite and calcite. Calcite exhibits the higher intensity than aragonite inside the sample, as marked in the XRD graph. From the SEM image, we can observe that the shapes are quite similar in those in Figure 4.3 (a), bulky and cylindrical in shape. Despite the inconsistency in shape, it can still be confirmed that the precipitate formed to be calcite and aragonite, by referring to the XRD analysis.

In addition, the level of the pH of the solution seems to be also dropping drastically at the end. The explanation is that carbon dioxide actually dissolved in the seawater. As the carbon dioxide is acidic, it lowers the alkalinity of the solution towards more acidic solution.

Furthermore, the amount of calcium carbonate formed inside the sample is comparatively lower compared with the previous experiment, approximately 1.85 g.

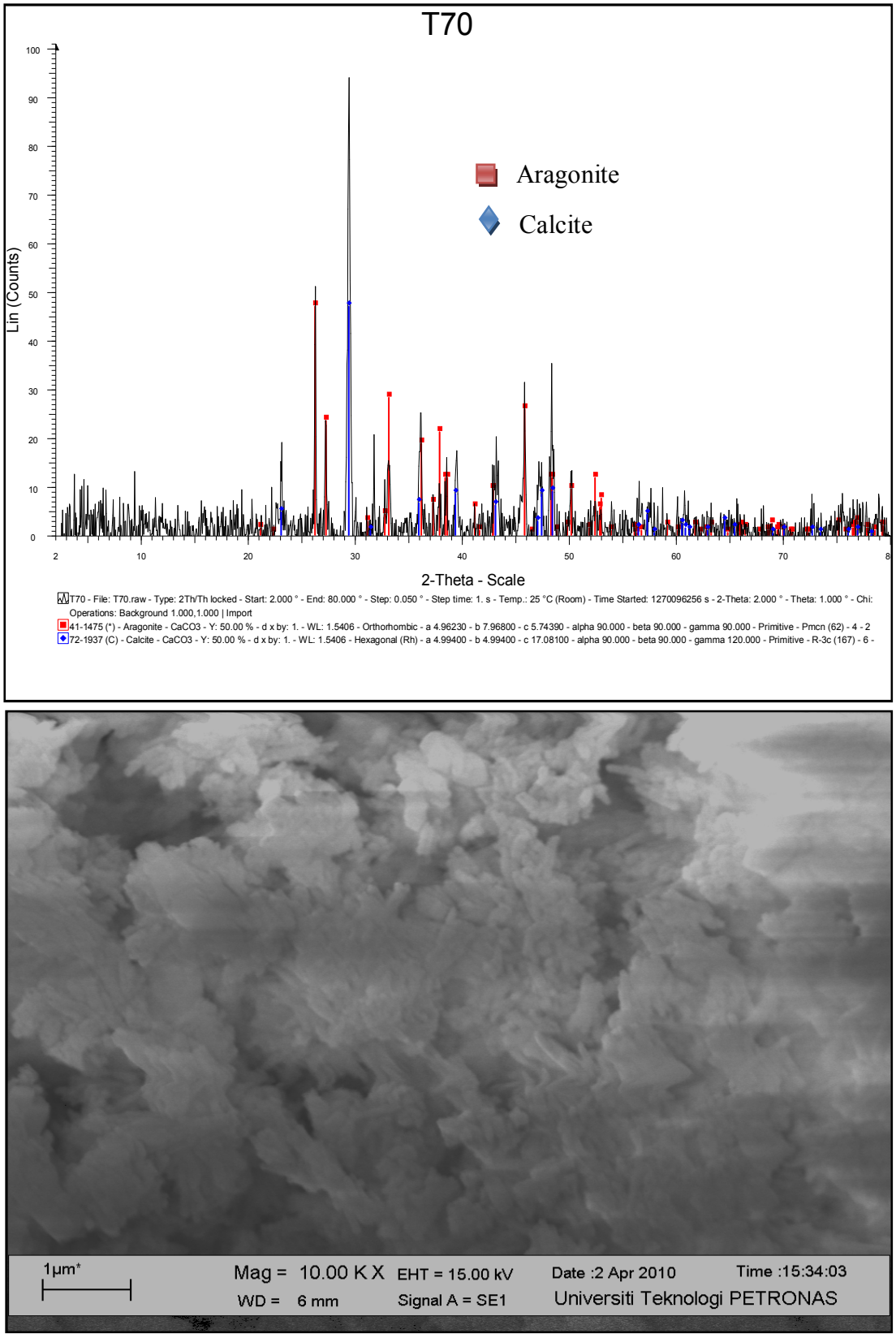


Figure 4.3 (c): XRD and SEM analysis at 70°C

Figure 4.3 (c) shows the results of XRD and SEM scanning of the sample run at 70°C. As expected, the XRD result shows that calcium carbonate was formed inside the flask in form of calcite and aragonite. However, at the temperature of 70°C, it can be observed from the XRD graph that the intensity of aragonite is generally higher than calcite that formed. None other elements are traced in the sample besides that and no trace of vaterite detected. However, referring to the SEM image, the shape of the precipitate formed comparatively much smaller than the previously samples, taking at the same level of magnification. Same as before, the shape is quite similar from the previous sample, but much smaller in size. Despite the inconsistency in shape, it can still be confirmed that the precipitate formed to be calcite and aragonite, by referring to the XRD analysis. In addition, the level of the pH of the solution seems to be dropping drastically at the end of the process. The explanation is that carbon dioxide actually dissolved in the seawater. As the carbon dioxide is acidic, it lowers the alkalinity of the solution towards more acidic solution.
Furthermore, the amount of calcium carbonate formed inside the sample is comparatively lower compared with the previous experiment, approximately 2.1 g only.

Nevertheless, despite the size difference and relatively small amount of $CaCO_3$ that forms, we can still conclude that CO_2 can actually sequestrated inside seawater to form $CaCO_3$ plus having direct effects from the temperature variation.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

From both of the experiments, we succeeded in sequestrating CO_2 naturally in seawater, forming $CaCO_3$. In addition, there is a relationship between temperature variation and the formation of $CaCO_3$, which are; at lower temperature (30°C), the formation of $CaCO_3$ is favored by calcite. As the temperature increases near to 50°C, aragonite started to form together with calcite however at lower concentration of aragonite. Finally, at 70°C, the formation of aragonite dominates over calcite as shown in the results.

In addition, the results of the experiment also show the relation between the activation energy and the rate of formation of calcium carbonate. High activation energy causes the rate of formation of calcium carbonate to be slightly increased.

Apart from that, there are other several parameters that might also affect the formation of $CaCO_3$ such as concentration, pH level and possibly pressure effects of the surroundings which may require additional studies.

There are however, several improvement can be made in terms of apparatus setup and methodology to further increase the accuracy and the reliability of the study. One of the recommendations is that to isolate the system and to properly measure the amount of carbon dioxide gas supplied throughout the process. By doing so, the exact amount of calcium carbonate formed and carbonate ion consumed can be calculated theoretically.

For the future development, with combined knowledge gained from the experiment, along with other parameters as mentioned earlier, we can ultimately construct a module or experiment that can produces $CaCO_3$ from highly available and cheap resources such as seawater along with optimum level of pH and temperature. It might be possible to use tap water as the main supply of calcium since tap water also contain calcium and the dissolved ions inside tap water is less complex compared to seawater.

Beneficial studies can be done to find a method on how to manipulate the concentration of calcium ion inside the seawater and also to increase the pH level of the seawater by using natural and cheap sources of alkaline material such as bitter gourd. Combining all the pieces together, the experiment or module might realizable to be done.

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